Green chemistry in sustainable national development^ψ

M. Kidwai* and R. Thakur

Department of Chemistry, University of Delhi, Delhi-110 007, India

E-mail : kidwai_chemistry@yahoo.co.uk Fax : 91-11-27666235

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The green chemistry revolution provides an enormous number of oppourtunities to discover and apply new synthetic approaches using alternative feedstocks; ecofriendly reaction conditions, energy minimizations and the design of less toxic and inherently safer chemicals. The origin and basis of green chemistry chart for achieving environmental and economic prosperity inherent in a sustainable world. One important element of sustainable chemistry is commonly defined as the chemical research aiming at the optimization of chemical processes and products with respect to energy and material consumption, inherent safety, toxicity, environmental degradability, and so on. While considerable progress has been made in environmental chemistry, green chemistry, and the environmental assessment of chemical products but the societal aspect of sustainable chemistry remains to be recognized fully in all branches of chemical research, one prerequisite for this is the inclusion of sustainable chemistry into chemical education from the very beginning.

Definition

Green Chemistry (environmentally benign chemistry) is the utilization of set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products. In practice, green chemistry is taken to cover a much broader range of issues than the definition suggests¹. As well as using and producing better chemicals with less waste, green chemistry also involves reducing other associated environmental impacts², including reduction in the amount of energy used in chemical processes. Green Chemistry is not different from traditional chemistry in as much as it embraces the same creativity and innovation that has always been central to classical chemistry. However, there lies a difference in that historically synthetic chemists have not been seen to rank the environment very high in their priorities. But with an increase in environmental consciousness throughout the world, there is a challenge for chemists to develop new products, processes and services that achieve necessary social, economical and environmental objectives. Since the types of chemicals and the types of transformations are much varied, so are the green chemistry solutions that have been proposed. Anastas and Warner³ (1998) developed 'The Twelve Principles of Green Chemistry' that serve as guidelines for practising chemists in developing and assessing how green a synthesis, compound, process or technology is.

Industrial interest in Green Chemistry

Many forward-looking companies are embracing green chemistry, not only to protect the environment and to create good public relations, but also because it is often beneficial to the bottom line^{4,5}. It is estimated to cost US industries between \$ 100 and \$ 150 billion per year the comply to environmental regulations⁶. In addition, cleaning up hazardous waste sites will cost hundreds of billion of dollars. In many companies, the cost of dealing with environmental regulations often exceeds their expenditures for research. Larger companies budget close to \$ 1 billion per year for environmental compliance. If a company can significantly reduce these expenditures, then these funds can be spent in more productive areas and result in an improved bottom line. Thus, green chemistry (pollution prevention) is not only good for the environment but also for industry.

Green Chemistry in Education

Convincing chemists to think in an environmentally friendly manner begins with education. The idea of including green chemistry in chemistry education was first put forward in 1994⁷. A complete course was described shortly thereafter⁸. Few green chemistry textbooks have also been published^{3,9}. Graduates, post-graduates, teachers and researchers will find these books of immense use. Both EPA and ACS have recognized the importance of bringing green chemistry to the classroom and the labo-

^ψDedicated to Professor H. C. Gaur on his 80th birthday.

ratory. Together they have launched a significant campaign to develop a green chemistry educational materials and to encourage the greening of the chemistry curriculum^{10,11}.

Student involvement in Green Chemistry principles and practices is essential to the integration of environmentally benign technologies in academia and industry. ACS Student Affiliate Chapters may be recognized as a "green" chapter by engaging in at least three green chemistry activities during the academic year. Suggestions for such activities include :

- Hosting a green chemistry speaker.
- Organizing an interdisciplinary green chemistry workshop on campus.
- Working with a local company on a green chemistry project.
- Developing a Green Chemistry activity with a local school.
- Converting a current lab experiment into a greener one.
- Organizing a Green Chemistry poster sessions on campus.
- Distributing a Green Chemistry Newsletter to the local community.
- Designing a Green Chemistry web-page.

Atom efficiency

One of the key ideas of green chemistry is that of atom economy. The concept of atom economy as developed by Barry Trost considers how much of the reactants in a chemical reaction ends up in the final useful product or products. With selectivity and yield being the prime concern in the areas of fine chemicals, pharmaceuticals and academics, the efficient use of reactants from the standpoint of atom economy is often ignored^{12,13}. When these reactants are used inefficiently their atoms wind up, in part, as waste byproducts of the reaction. The goal of atom economy is to create syntheses in which most of the atoms of the reactants become incorporated into the desired final product leading to fewer waste byproducts¹⁴.

The concept of atom economy was quantified by Sheldon¹⁵ (Professor at Delft University in the Netherlands). He calculated percentage atom utilization by dividing the molecular weight of the desired product by the molecular weights of all the products generated in a reaction (Formula 1).

$$\% \text{ Atom utilization} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight (desired product + waste by products)}} \times 100$$

Formula 1

However, in many reactions the identities of waste by products are unknown or difficult to determine. Fortunately, conservation of mass can be used to calculate a number similar to the percentage atom utilization called the percentage atom economy by totaling the formula weight (FW) of all the atoms in the reactants that are incorporated into the final products and divide this number by the total formula weight of all the reactants (Formula 2).

$$\% \text{ Atom economy} = \frac{\text{Formula weight of atoms utilized}}{\text{FW of all reactants used in the reaction}} \times 100$$

Formula 2

When we look at some common organic reactions (rearrangement, addition, substitution and elimination) we find that the rearrangement and addition reactions tend to be most atom economical (100%), followed by substitution (65.41%) and the least economical being the elimination reaction (35.30%) (Schemes 1-4).

$$\% \text{ Atom economy} = \frac{134.175}{134.175} \times 100 = 100\%$$

Scheme 1. Claisen rearrangement.

$$\% \text{ Atom economy} = \frac{44.096}{44.096} \times 100 = 100\%$$

Scheme 2. Addition reaction.

$$\% \text{ Atom economy} = \frac{87.120}{133.189} \times 100 = 65.41\%$$

Scheme 3. Substitution reaction.

$$\% \text{ Atom economy} = \frac{42.080}{119.205} \times 100 = 35.30\%$$

Scheme 4. Elimination reaction.

Many atom economical reactions using various transition metal catalysts have been developed^{16,17}. The synthesis of rosefuran¹⁸ (Scheme 5) performed using metal transition complexes in catalytic cycle, is example of an atom economic process proceeding with very high yield and substantial waste reduction. The concept of atom economy has also been employed by the Shell corporation to make methyl methacrylate (Scheme 6)¹⁹. The old synthesis (Scheme 7) manifests only 47% atom economy due to the use of stoichiometric amounts of hydrogen cyanide and sulfuric acid whereas the new synthesis (Scheme 6), which employs a palladium catalyst, enjoys 100% atom economy. Recently many classical routes for chemical synthesis are being replaced by catalytic processes²⁰. Scheme 8 compares the synthesis of acetophenone by classical oxidation of 1-phenylethanol using stoichiometric amounts of chromium oxide and sulfuric acid, resulting in an atom efficiency of 42%, with the heterogeneous catalytic oxidation with O₂, having an atom efficiency of 87% and resulting in water as the only byproduct. The increasing use of catalytic processes can substantially reduce waste at the source resulting in primary pollution prevention.

Scheme 5

Scheme 6

Scheme 7

Stoichiometric oxidation

Catalytic oxidation

Scheme 8

Energy conservation

Energy generation and consumption has long been known to produce a major environmental effect. Chemistry and chemical transformations play a major role in capturing and converting substances into energy as well as converting existing sources of energy into a form that is usable to society. Microwave irradiation in the solid state²¹ is a technique that is being utilized to effect chemical transformations rapidly, in contrast to those that have classically been conducted in liquid solutions. Solvent-free microwave assisted reactions²² provide an opportunity to work with open vessels thus avoiding the risk of high pressure and increasing the potential for scale up of such reactions. The practical feasibility of microwave assisted solvent free synthesis has been demonstrated in various useful transformations²³⁻²⁵ and in the synthesis of heterocyclic systems²⁶⁻²⁸ (Schemes 9-11). The microwave technique has shown distinct advantages in not requiring prolonged heating to carry out a reaction.

Scheme 9

Scheme 10

Scheme 11

Ultrasound is a relatively new way of introducing energy into chemical systems²⁹. It has been used to enhance reaction rates³⁰ in a large number of classical organic reactions (Scheme 12). Though the use of phase transfer catalysts in organic aqueous biphasic systems is well known to catalyse heterogeneous liquid-liquid reactions, ultrasound is much more effective in these reactions because ultrasonic waves generate extremely fine emulsions which results in very large interfacial contact areas between the liquids and a corresponding dramatic increase in the reactivity between dissolved species (Scheme 13).

Scheme 12

Scheme 13

The problems associated with waste disposal of solvents and excess chemicals has been overcome by performing reactions without solvent under microwave irradiation (MWI) or ultrasound. Heterogeneous organic reactions have also proven useful to chemists. These reactions are effected by the reagents immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of good dispersion of active reagent sites, associated selectivity and easier work up.

Green alternatives

Two of the main components of chemical synthesis are feedstocks and reaction conditions : either or both of these may be changed to produce alternative or improved chemical syntheses. With advances in biotechnology, biocatalysis and biosynthesis there have been significant accomplishments in the use of biologically based feedstocks/raw materials as a viable alternative to petroleum feedstocks for a number of chemical processes³¹. The selection of feedstocks has a major effect, not only on the efficacy of the synthetic pathway, but also on the environmental and health effects of the process. Like many chemicals, adipic acid, catechol and BHT are produced using petroleum-based starting materials, namely benzene and toluene. Draths and Frost^{32,33} have developed a biosynthetic method to produce adipic acid, catechol and DHS from glucose in place of benzene using genetically

altered *E. coli* (Scheme 14). This biosynthetic pathway can help to minimize the use of certain reagents with significant toxicity.

Scheme 14

Reagents :

In particular, an underdeveloped area of chemistry involves the replacement of reagents which are toxic, dangerous, produced by eco-unfriendly processes and not selective. In order to carry out the transformation of selected feedstocks into the target molecule, the criteria efficiency, availability and effect of the reagent used must be kept in mind. Examples of undesirable reagents used for methylation and carbomethylation are methyl halides (CH_3X), dimethylsulfate (DMS) and phosgene. These toxic and waste producing reagents have a valuable green alternative i.e. dimethylcarbonate (DMC). Tundo³⁴ has used DMC as an environmentally benign substitute for DMS and CH_3X in methylation reactions (Scheme 15). The traditional synthesis of polyurethanes requires the use of phosgene, an extremely toxic gas. The Monsanto company has developed a method of synthesizing polyurethanes that totally eliminates the use of phosgene³⁵ (Scheme 16).

Scheme 15

Scheme 16

K_2CO_3 has been used as a green reagent^{36,37} for the synthesis of various heterocyclic compounds (Schemes 17–19). The usage of K_2CO_3 not only eliminates the requirement of solvent from reaction stage but work up requires only water. Also K_2CO_3 serves as a base, eliminating the need for an external base.

Solvents :

Scheme 17

Scheme 18

Scheme 19

An important area of green chemistry investigations has centered around the selection of a medium in which to carry out a synthetic transformation. Many of the solvents commonly used are volatile organic compounds known to cause smog when released in air. These solvents are listed in the United States' Clean Air Act as substances to be avoided. There has been an increased emphasis, both in the chemical industry and academic research on development of environmentally benign solvents. While traditional solvents are well known, alternatives such as ionic liquids and supercritical fluids are increasingly being applied in synthesis. Usage of supercritical fluids, such as carbon dioxide, not only obviate waste disposal problems but also offer other advantages³⁸ such as controlling the phase behaviour of products, increasing reaction rates and providing better efficiency. Supercritical carbon dioxide³⁹ has been employed in the synthesis of organometallic compounds, metal chelation, extractions, preparation of nanoparticles and lipase-catalysed reactions.

As a result of the compelling need for industry to consider the reengineering of entire processes, ionic liquids have begun to receive worldwide academic and industrial attention⁴⁰. Ionic solvents provide a unique opportunity for science/engineering/business to work together from the beginning of a field's development and thus lead more quickly to innovative environmentally and economically sustainable industrial processes. General advantages of ionic solvents are that they have no measurable vapour pressure, are thermally robust, will tolerate impurities such as water and if the extraction solvent is recycled, generate almost no waste product.

'Neat critical' water offers outstanding performance

as a benign solvent for both organic and ionic compounds⁴¹. Conventionally, Friedel-Crafts acylations require the presence of Lewis acids such as aluminium chloride, ferric chloride and zinc chloride. But in neat critical water, phenol could be converted with acetic acid to produce 2'-hydroxyacetophenone, 4'-hydroxyacetophenone and phenyl acetate without the addition of an acid catalyst (Scheme 20).

Scheme 20

Catalyst :

Some of the major advances in chemistry, especially industrial chemistry, over the past generation have been in the area of catalysts. Through the use of catalyst, chemists have found ways of removing the need for large quantities of reagents that would otherwise have been needed for chemical transformation and would ultimately have contributed to the waste stream. For example, the traditional catalyst hydrogen fluoride, an extremely corrosive, hazardous and toxic chemical used in the production of linear alkylbenzenes (LAB's), has been successfully replaced by a solid acid catalyst, viz. fluorided silica-alumina catalyst, which does not require special construction materials, involves lower operating costs and obviates the need for waste disposal of calcium fluoride³.

Biocatalytic transformations represent an immense potential in organic synthesis. Enzymes occupy a prominent place among biocatalysts and have a wide spectrum of biotechnological applications⁴². The stability of enzymes in organic solvents have pushed them into the frontier areas of organic synthesis⁴³.

An environmentally friendly and safe method developed for preparation of 3-carbamoyl cephalosporin derivatives, such as cefuroxime and its prodrug ester, cefuroxime axetil uses *o*-transcarbamoylase, an enzyme of microbial origin for the conversion of the 3-hydroxy function to the desired 3-carbamoyl group. This new synthesis replaces the conventional chemical route, that em-

plays hazardous isocyanates such as dichlorophosphinyl isocyanate or chlorosulfinyl isocyanate⁴⁴ to achieve the same conversion (Scheme 21).

R = H, acyl group

R¹ = H or carboxyl protective group

Scheme 21

More than 90% of all processes in the chemical and petrochemical industry as well as in refinery technology are mainly *heterogeneously catalyzed* processes. A large number of industrial process which are catalyzed by solid acid, base and acid base bifunctional catalysts are known. Zeolites themselves account for more than 40% of the acid-base catalysts. As an example, isobutene reacts with ammonia over pentasil zeolites at 300°C and 300 bar to give excellent results⁴⁵ (Scheme 22).

Scheme 22

Phase transfer catalyst (PTC) :

The PTC methodology is applicable to a great variety of reactions in which inorganic and organic anions and also carbenes react with organic substrates. PTC in liquid-solid systems is often used for synthesis and manufacturing of esters of carboxylic acids via reaction of solid sodium or potassium carboxylates with alkyl halides⁴⁶ (Scheme 23).

Scheme 23

While a synthesis is often driven by the pursuit of a particular target, with pharmaceuticals, the object is to maximize the therapeutic benefits of a molecule while minimizing or eliminating the toxic side effects. In cases where function is the primary motive, molecular manipulation that preserves efficacy of function by mitigating toxicity or other hazards is the goal of green chemistry. Through these efforts and other toxicological research, it

is often possible to identify the part or parts of a molecule that produce toxic effects. An example of how one can assess the toxicological consequences of a particular functional group and then use this information to design inherently safer compounds has been described by De Vito⁴⁷ who compared the toxicity of 3-hydroxypropionitrile vs 2-hydroxypropionitrile (Fig. 1).

Fig. 1

Toxicological studies demonstrate that the 2-hydroxy isomer is much more toxic than the 3-hydroxy isomer. The mechanism of acute toxicity is proposed to be elimination of hydrogen cyanide from the cyanohydrin. Depending on the nature of the substitution at the α-carbon, this elimination can be accelerated or slowed down. Knowing this, new propionitriles can be designed to reduce this mechanistic pathway and thus be inherently safer⁴⁸. Reacting aryl acetonitriles with dimethyl carbonate at 180–220°C in presence of K₂CO₃ produces 2-aryl propionitriles with high selectivity (>90%). In this process no inorganic salts are produced (Scheme 24).

Scheme 24

Sustainable Chemistry : Starting points and prospects

Sustainability is significantly determined by how we manipulate matter within the economy, the inventive leadership of chemists is vital to its future⁴⁹ sustainable chemistry should also address the societal aspect of sustainability, with respect to scientific research, the societal aspect is designed by two requirements :

- (1) The assumptions, objectives and implication of chemical research and its technical application should be made more transparent to various societal actors.
- (2) Uncertainty and ignorance should be treated more explicitly in the course of scientific research.

Current status

Since 1991, green chemistry has grown into a significant internationally engaged focus area within chemistry. Research programs and centres located in America, Europe, Asia/Pacific and Africa are focusing efforts around the principles of green chemistry⁵⁰. The breadth of this research is very wide and incorporates area such as

- (I) Bio-based renewables
- (II) Green engineering education for sustainability for developing countries
- (III) Compressed CO₂ an environmentally friendly solvent
- (I) Bio-based renewables :

The utilization of benign, renewable feed stocks is needed component of addressing the global depletion of resources. Bio-based products hold great promise for achieving the goals of sustainable development and implementing the principles of industrial ecological and green chemistry⁵¹.

Achieving a sustainable chemical industry dictates switching from depleting finite sources to renewable feed stocks.

Research in this area has focused on both the macro and molecular levels.

- (1) The carbohydrate economy provides a rich source of feed stock for synthesizing commodity⁵² and for example :

- (2) Shells from crabs and other sea life serve as a valuable and plentiful source of chitin which can be processed into chitosan • a biopolymer with a wide range of potential applications that are being currently explored for use in the oil-drilling industry⁵³.
- (3) Genetic engineering produces valuable chemical products via nontraditional pathways.
- (4) Glucose $\xrightarrow{\text{Yields}}$ Catechol and adipic acid⁵⁴.
- (5) Saccharomyces yeasts convert both glucose and

(a) *E.coli* AB 2834/pKD 136/pKD 9.069 A. 37°C

xylose, present in cellulosic biomass, into ethanol⁵⁵.

- (6) CO₂ is also a renewable feedstock that has been incorporated into polymers⁵⁶.

(II) Green engineering education for sustainability for developing countries :

Ujang *et al.*⁵⁷ presented a paper of existing philosophy, approach, criteria and delivery of environmental engineering (EE) education (E₃) for developing countries.

(1) In general EE is being taught in almost all major universities in developing countries, mostly under civil engineering degree programmes. The main component of E₃ in near future will remain on basic sanitation in most developing countries, with special emphasis on the consumer-demand approach.

(2) The concept, principles and methodologies of Green chemistry and Green engineering are fundamental in integrating sustainability⁵¹ throughout the system of our chemical enterprise. By incorporating these Green chemistry approaches in the research and development, scale-up and commercialization stages in industry and by ensuring that training of both established and next generation chemists and engineers includes Green chemistry and engineering, large strides can and are being made in sustainability in the chemical industry.

(3) In order to substantially overcome environmental problems in developing countries, E₃ should include integrated urban water management, sustainable sanitation, appropriate technology, cleaner production waste water minimisation and financial framework.

(III) Compressed CO₂ an environmentally friendly solvent :

Many solvents are unpleasant but essential industrial chemicals. Supercritical CO₂ would be a viable green alternative but its use has been restricted by its limited solvent power. This is about to change.

Phase diagram for CO₂

Beyond a specific temperature and pressure CO₂ becomes a supercritical fluid, a state that is neither a gas nor a liquid, but has properties of both, known as critical point.

- (1) The specific properties of ScCO₂ make it an interesting "green" replacement for organic solvent which are often less than ideal owing to their acute toxicity, ecological hazards or difficulty with disposal and recycling.
- (2) Supercritical CO₂ (ScCO₂) find applications in areas as diverse as the dyeing and cleaning of fibres and textiles polymerization and polymer processing, purification and crystallization of pharmaceuticals, and last but not the least as a reaction medium for chemical synthesis.
- (3) Most widely used CO₂ Philic solubilizer have been polysiloxanes and fluoro-carbons. The Beckman group⁵⁸ has now synthesized a non-fluorous but still highly CO₂-philic polymer, whose solubility in ScCO₂ results from a judicious design.
- (4) The target compound of the Beckman group was copolymer (polyether and polycarbonate group) such copolymers can be easily generated using an Al-catalyst to react propylene oxide (C₃H₆O) with CO₂ itself.
- (5) Polyether skeleton is highly flexible and has only weak polymer-2 interactions, when carbonate group is introduced. It enhances this flexibility, and therefore the entropy of mixing. At the same time a favourable interaction of the carbonyl group with CO₂ may increase the enthalpy of mixing, thereby also improving the solubility of these compounds in CO₂.

Conclusion :

The growth of green chemistry over the course of the past decade needs to increase at an accelerated pace if molecular science is to meet challenges of sustainability. It has been said that the revolution of one day becomes the new orthodox of the next Green chemistry is applied and must involve the successful implementation of more environmentally friendly chemical processes and product

design. Most importantly we need the relevant scientific, engineering, educational and other communities to work together for sustainable future through Green chemistry.

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